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**MIGRATION OF CREOSOTE AND ITS COMPONENTS FROM
TREATED PILING SECTIONS IN A MARINE ENVIRONMENT**

--FINAL REPORT--

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MIGRATION OF CREOSOTE AND ITS COMPONENTS FROM TREATED PILING SECTIONS IN A MARINE ENVIRONMENT

INTRODUCTION

Migration of creosote and its components from treated wood products in a marine environment is a phenomenon that has received attention for many years because of its long-term effect on service life. More recently, this problem has been accorded a new level of urgency as a result of recent research findings which suggest that the loss of creosote oil from marine structures constitutes an environmental and public health hazard. The increased environmental concern is due to the fact that creosote oil consists of 50% polycyclic aromatic hydrocarbons (PAH), such as fluorene, fluoranthene, chrysene, pyrene, and phenanthrene.

The EPA has established a list of toxic substances which are either known or are likely to be present in selected aqueous effluents. Ultimately, the EPA is bound under a consent decree to establish a monitoring program with the intent to control the concentration of such substances in the effluents at an environmentally acceptable level. These toxic substances have been categorized on a chemical basis into 13 categories. One of these categories contains 16 polynuclear aromatic hydrocarbons which are to be monitored in industrial aqueous effluents. They range from two-ring compounds such as naphthalene to six-ring compounds (benzo(g,h,i)perylene). The group contains known and suspected carcinogens such as benzo(a)pyrene and benzo(b)fluoranthene, as well as noncarcinogens such as the isomer benzo(k)fluoranthene. These PAH compounds which are to be monitored under this consent decree

program are: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. Creosote contains all sixteen PAH which are on the EPA's priority pollutant list; it contains major amounts of acenaphthene, phenanthrene, fluorene, fluoranthene, and pyrene (Table 1). The most important environmental concern is the ultimate fate of the PAH in wood during exposure to the environment. In other words, how much remains in the wood and how much migrates to the environment.

The available evidence, which is limited and not very conclusive, indicates that the amounts of PAH entering the atmosphere from treated wood in service are relatively small. This assumption is based on the long-term service life of creosote-treated materials, the lack of reported evidence of adverse health or environmental problems from creosote-treated material over the last 125 years, and the finding that poles and pilings still retained high amounts of creosote after 20 - 50 years of service (2 - 6).

The level of creosote oil in aging piling is determined by the extraction and assay of borings at irregular and widely spaced time intervals using a non-specific procedure that gives information only about the total amount of creosote oil present. While such data provide an indication of the rate of oil loss, they do not adequately address the question of the rate of migration, concentration, and identity of the specific constituents of creosote that enter the aquatic environment. The purpose of this work was to provide baseline data on the rate of loss of both

Table 1. .Chemical Composition of Creosote (1).

Compound or Component	Concentration (%)
Naphthalene ^a	3.0
Methyl Naphthalene	2.1
Biphenyl	0.8
Acenaphthene ^a	9.0
Dimethylnaphthalenes	2.0
Dibenzofuran	5.0
Fluorene ^a	10.0
Methyl Fluorenes	3.0
Phenanthrene ^a	21.0
Anthracene ^a	2.0
Carbozole	2.0
Methylphenanthrenes	3.0
Methylanthracene	4.0
Fluoranthene ^a	10.0
Pyrene ^a	8.5
Benzofluorenes	2.0
Chrysene ^a	3.0

^aEPA priority pollutants.

creosote oil and selected polynuclear aromatic hydrocarbons from treated wood in a marine environment and to provide a better basis than that currently available for assessing the environmental and health hazards that such losses represent. More specifically, the purpose of this study was to expand the data base available on the rate of migration of creosote and a selected number of its constituents from treated wood in a marine environment. Specific objectives were as follows:

1. Determine the identity and rate of loss from piling sections of those constituents of creosote currently included in EPA's list of priority pollutants, primarily the polynuclear aromatic hydrocarbons.
2. Ascertain the effect of duration of exposure in a marine environment on both rate of loss and composition of the polynuclear hydrocarbon fraction.
3. Determine if an identifiable relationship exists between the loss of whole oil and the loss of specific chemical constituents of creosote.
4. Compare the effect of fresh water and sea water on the loss of creosote and its constituents from piling sections.

PROCEDURE

Materials

The sample pilings used were creosote-treated marine pilings. The unaged marine pilings were prepared from kiln-dried, class five, machine-shaved southern pine poles (Pinus sp.) and treated to a retention of 22.1 - 23.6 pcf. After treatment the wood was stored for approximately six months in the open air before being used in this study. The aged samples were a group of treated marine pilings which had been exposed to sea water at Key West, Florida, since their installation in December, 1968. The creosote retention in these pilings varied from 27.6 to 37.2 pcf (7). The sea water was collected at Alabama City, Alabama, from the Gulf of Mexico.

Experimental Conditions

Two separate units were used in leaching studies; a 300-gallon stainless steel tank and 4-liter glass beakers.

Tank Studies - Sections of pilings with an exposed lateral surface area of 513 - 3375 cm² were end coated with an epoxy resin and used in this study. The 300-gallon stainless steel tank was filled with 200 - 250 gallons of sea water and a piling was placed in the vessel. The tank was sealed and the sea water was stirred continuously. The temperature was controlled at 18 - 20°C during the runs.

Two-liter water samples were removed daily and initially filtered using #541 hardened ashless filter paper. The samples were then pumped through two columns in series packed with Waters C-18 reverse phase material (Waters Associates C-18 Sep-Paks) in order to remove the dissolved organic components from the water. The water was discarded and the trapped PAH on the column were removed by flushing the column with 30 ml of HPLC-grade acetonitrile. The acetonitrile was removed using a rotary evaporator. The sample was dissolved in 1 ml of hexane which contained 100 ppm of 1-chlorotetradecane, an internal standard. Two microliters of this sample were injected on a Perkin-Elmer Model 900 gas-chromatograph using a 30-meter GSC/SP 2100 glass capillary Scot column with 0.5 mm id. The chromatographic conditions are given in Table 2.

The data were collected and analyzed using a Perkin-Elmer Sigma 10 data system. The efficiency of the collection and analysis system for some standard solutions of PAH in water is shown in Table 3.

Table 2. Gas Chromatographic Conditions.

Injector Split Ratio (Actual)	2.2/1
Manifold Temperature	250°C
Injector Temperature	250°C
Temperature Program	
Initial Temperature	100°C
Initial Time	2 min.
Program Rate	4°/min.
Final Temperature	240°C

Table 3. Extraction Efficiency for Removing Low Levels of PAH from Aqueous Solutions.

Compound	Initial Concentration in Water/ Acetonitrile (ppm)	Recovery (%)
Chrysene	0.474	95.0
Chrysene	30.64	89.7
Phenanthrene	0.766	96.7
Phenanthrene	9.48	93.4
Fluorene	0.488	93.6
Fluorene	5.74	97.3
Acenaphthene	0.574	87.4
Acenaphthene	9.76	90.4

Beaker Studies - The leaching studies were also done in 4-liter beakers. The amount of creosote lost from sections of piling with 60 - 70 cm² of lateral surface was determined. Each section was end coated with epoxy resin before being used. These studies were done at temperatures within the range of 20 - 40°C using sea water, boiled sea water, and distilled water and using aged and unaged pilings. The beaker temperature was controlled ($\pm 0.5^\circ\text{C}$) using a Magni-Whirl constant temperature water bath. Samples (500 ml) were withdrawn from the beaker, processed, and analyzed using the procedure previously described.

Solubility Studies - Duplicate samples of creosote oil (150 ml) were stirred in 2 liters of sea water at 25°C in order to determine the solubility of the creosote components in this medium. The stirring was continued for three days, the stirring stopped, and the sample allowed to settle for several days. The liquid sample (500 ml) was then withdrawn, filtered, and the total dissolved components were determined using the procedure described previously. The process was repeated using fresh water instead of distilled water.

Creosote Composition of Wood - Creosote-treated wood was ground to 2 mm in a Wiley mill. Duplicate samples (1.00 g) were placed in a round-bottom flask, 50 ml of cyclohexane was added, and the sample was placed in an ultrasonic unit for exactly 15 minutes. The solution was filtered and diluted to 100 ml with cyclohexane. A sample (1 ml) of the solution was evaporated to dryness and dissolved in 1 ml of hexane containing 100 μg of 1-chlorotetradecane. This sample was analyzed using the procedure previously described.

RESULTS AND DISCUSSION

The major PAH components which migrated from creosote-treated wood into water were naphthalene, phenanthrene, acenaphthylene, dibenzofuran, fluorene, and 2-methylnaphthalene. These six components make up approximately 78% of the total PAH that migrated into the water from nonaged pilings. Table 4 shows the relative percentages of the 15 major PAH in creosote-treated wood after three days of leaching. It was found that all of the PAH in the wood, with the exception of chrysene, migrated into the water. However, a much higher percentage of the lower-molecular-weight PAH, such as naphthalene and acenaphthylene, were found in the water as compared to their percentage in wood. For example, 2-methylnaphthalene (mw = 142) makes up 5.86% of the PAH in wood, but comprised 9.62 - 9.67% of the PAH migrating into the water. In contrast, fluoranthene (mw = 202) makes up 10.44% of the PAH in wood, but comprised only 1.57 - 1.61% of the PAH migrating into the water. This effect is probably due to the decreased solubility of the higher-molecular-weight PAH in water.

The temperature and the type of aqueous solution (sea water or fresh water) also have a major effect on the rate of migration of the PAH from treated wood (Tables 5 - 7). At 20 - 40°C, the major PAH components that migrated from unaged wood into water were naphthalene, acenaphthylene, phenanthrene, dibenzofuran, fluorene, and 2-methylnaphthalene. The total concentration of the 15 major PAH in water was 1287 - 1735 ppb at 20°C, 1984 - 2864 ppb at 30°C, and 2599 - 3479 ppb at 40°C. When sea water was used as a solvent, the amount of PAH that migrated from the wood was considerably lower. The total amount of PAH which was leached from the wood into the water was 384 ppb at 20°C. This value increased to 742 - 1393 ppb at 30°C and 1813 - 2373 ppb at 40°C.

Table 4. Relative Percentages of the Major PAH in Wood and in Water After Three Days' Immersion.^a

Compound	Treated Wood	Water ^b	
	(%)	(%) ^c	(ppb)
Naphthalene	19.60 ✓	16.4 - 22.8	454 - 471
2-Methylnaphthalene	5.68 ✓	9.62 - 9.67	191 - 277
1-Methylnaphthalene	2.55	4.43 - 4.96	88 - 142
Biphenyl	1.74	2.65 - 3.52	70 - 76
Acenaphthene	1.51	3.07 - 3.28	61 - 94
Acenaphthylene	7.65 ✓	13.69 - 13.71	272 - 392
Dibenzofuran	5.74 ✓	9.88 - 10.19	196 - 292
Fluorene	6.38 ✓	9.27 - 11.00	184 - 315
Phenanthrene	23.55 ✓	14.4 - 17.11	286 - 490
Anthracene	5.10	4.33 - 4.89	86 - 140
Carbazole	2.32	2.06 - 2.62	41 - 75
Fluoranthene	10.44	1.57 - 1.61	32 - 45
Pyrene	6.32	0.76 - 1.60	15 - 46
1,2-Benzanthracene	0.29	0.31 - 0.39	7.8 - 8.9
Chrysene	1.10	-- - --	-- - --

^aConditions for this study were:
 Exposed Surface Area = 54.37 - 63.3 cm².
 Water Volume = 3500 ml
 Temperature = 30.0°C ± 0.5%.

^bAfter three days' immersion.

^cEach value represents an average of two runs.

Table 5. Effect of the Solvent on the Migration of Creosote from Treated Wood at 20°C.^a

Compound	Fresh Water ^{b,c} (ppb)	Sea water ^{b,c} (ppb)
Naphthalene	198 - 348	78
2-Methylnaphthalene	169 - 178	26
1-Methylnaphthalene	79 - 87	15
Biphenyl	46 - 57	9.1
Acenaphthene	51 - 68	16
Acenaphthylene	194 - 231	47
Dibenzofuran	138 - 168	30
Fluorene	117 - 148	52
Phenanthrene	190 - 225	51
Anthracene	48 - 76	--
Carbazole	7.2 - 88	5.5
Fluoranthene	27 - 30	5.1
Pyrene	12 - 12	5.4
1,2-Benzanthracene	11 - 19	44
	1510	384

^aSample used had: Exposed Area = 52.75 - 60.04 cm².
 Water Volume = 3500 ml.
 Temperature = 20 ± 0.5°C.

^bThese values were obtained after three days' immersion.

^cEach value represents an average of two runs.

Table 6. Effect of the Solvent on the Migration of Creosote from Treated Wood at 30°C.^a

Compound	Fresh Water ^{b,c} (ppb)	Sea water ^{b,c} (ppb)
Naphthalene	454 - 471	4.8 - 55
2-Methylnaphthalene	191 - 277	27 - 91
1-Methylnaphthalene	88 - 142	12 - 47
Biphenyl	70 - 76	23 - 29
Acenaphthene	61 - 94	24 - 43
Acenaphthylene	272 - 392	146 - 147
Dibenzofuran	196 - 292	115 - 167
Fluorene	184 - 315	145 - 163
Phenanthrene	286 - 490	214 - 323
Anthracene	86 - 140	0 - 137
Carbazole	41 - 75	21 - 68
Fluoranthene	32 - 45	4.2 - 59
Pyrene	15 - 46	6.4 - 58
1,2-Benzanthracene	7.8 - 8.9	0 - 6.2
	1487 2864 1124 2424	742 1393 1067 2

^aSamples used had: Exposed Surface Area = 54.37 - 63.07 cm².
Water Volume = 3500 ml.
Temperature = 30 ± 0.5°C.

^bThese values were obtained after three days' immersion.

^cEach value represents an average of two runs.

Table 7. Effect of the Solvent on the Migration of Creosote from Treated Wood at 40°C.^a

Compound	Fresh Water ^{b,c} (ppb)	Sea water ^{b,c} (ppb)
Naphthalene	373 - 596	147 - 263
2-Methylnaphthalene	161 - 244	89 - 144
1-Methylnaphthalene	73 - 105	43 - 65
Biphenyl	53 - 97	34 - 56
Acenaphthene	51 - 87	34 - 60
Acenaphthylene	253 - 390	173 - 267
Dibenzofuran	204 - 316	144 - 243
Fluorene	254 - 320	192 - 240
Phenanthrene	660 - 679	488 - 547
Anthracene	162 - 173	128 - 153
Carbazole	179 - 252	154 - 166
Fluoranthene	106 - 140	95 - 100
Pyrene	69 - 123	69 - 79
1,2-Benzanthracene	1.4 - 30	2.5 - 7.0
	2599 - 3552	1792 - 2390

^aSamples used had: Exposed Surface Area = 50.8 - 64.81 cm².
 Water Volume = 3500 ml.
 Temperature = 40° ± 0.5°C.

^bThese values were obtained after three days' immersion.

^cEach value represents an average of two runs.

Initially it was believed that the large difference in results between fresh water and sea water was due to the decreased solubility of organic compounds in sea water, which contains a high concentration of inorganic salts. The maximum solubility of creosote components in fresh water and sea water was determined by a series of experimental studies. A large excess of creosote oil was stirred for three days in both solvents. The excess creosote was removed and the amount of the dissolved creosote components was determined (Table 8). It was found that all 15 PAH were less soluble in sea water than fresh water; however, the difference between the solubilities of whole creosote in fresh water and sea water was much less than the difference observed between the concentrations of PAH from treated wood in sea water and fresh water. Apparently, there are other factors that may account for the decreased rate of migration.

The data from Table 8 also indicate that solubility was not a limiting factor in this study. The concentrations of PAH that migrated from treated wood (Tables 5 - 7) were much lower than the solubility of the PAH in fresh and sea water.

The effect of piling age on rate of migration of creosote components is shown in Table 9. The major PAH components which migrated from wood were acenaphthylene, phenanthrene, fluorene, dibenzofuran, and fluoranthene. These five components made up between 79 - 80% of the total PAH which migrated from the aged wood. There was considerably less PAH migration from the aged samples than from the non-aged samples, even though the aged wood samples contained a substantially larger amount of creosote. Table 10 gives the PAH contents of the non-aged and aged material used in this study. The aged piling contained 20.64 - 28.94% of the 15 PAH, while the non-aged material contained 17.24%.

Table 8. Solubility of PAH from Whole Creosote in Fresh Water and Sea Water.^a

Compound	Fresh Water (ppb)	Sea Water (ppb)
Naphthalene	3342 ± 452	1158 ± 371
2-Methylnaphthalene	1151 ± 109	784 ± 163
1-Methylnaphthalene	982 ± 80	784 ± 123
Biphenyl	196 ± 7	155 ± 27
Acenaphthene	256 ± 69	238 ± 3
Acenaphthylene	688 ± 88	640 ± 107
Dibenzofuran	482 ± 40	463 ± 47
Fluorene	405 ± 33	388 ± 44
Phenanthrene	660 ± 30	620 ± 70
Anthracene	168 ± 23	135 ± 21
Carbazole	368 ± 19	207 ± 35
Fluoranthene	184 ± 36	124 ± 20
Pyrene	103 ± 28	59 ± 6
1,2-Benzanthracene	43 ± 20	25 ± 12
Chrysene	36 ± 12 9064	9.7 6087

^a Approximately 150 ml of creosote oil was stirred in 2 liters of fresh water or sea water for three days at temperature of 22°C.

Table 9. Effect of Long-Term Aging on Creosote Migration in Sea Water.^a

	Concentration ^{b,c} Aged Piling (ppb)	Concentration ^{b,c} Unaged Piling (ppb)
Naphthalene	7.7 - 42	4.8 - 55
2-Methylnaphthalene	20 - 21	27 - 91
1-Methylnaphthalene	12 - 17	12 - 47
Biphenyl	4.1 - 20	23 - 29
Acenaphthene	6.9 - 19	24 - 43
Acenaphthylene	58 - 128	146 - 147
Dibenzofuran	57 - 95	115 - 167
Fluorene	64 - 134	145 - 163
Phenanthrene	28 - 211	214 - 323
Anthracene	0 - 31	0 - 137
Carbazole	1.9 - 4.6	21 - 68
Fluoranthene	23 - 77	4.2 - 59
Pyrene	8.8 - 15	6.4 - 58
1,2-Benzanthracene	---	0 - 6.2
Chrysene	0 - 22	26 - 47
	292 564 837	768 1104 1440

^aSamples used had: Exposed Surface Area = 54.4 - 79.07 cm².
 Sea Water Volume = 3500 ml.
 Temperature = 30°C ± 0.5°

^bThese values were obtained after three days' immersion.

^cEach value represents an average of two runs.

Table 10. Composition of Creosote in Marine Piling.

	Unaged Pilings (%)	Aged Pilings			
		#1	#2	#3	#4
		(%)			
Naphthalene	3.38	4.62	2.76	2.94	3.64
2-Methylnaphthalene	.98	2.19	1.52	1.44	1.85
1-Methylnaphthalene	.44	.92	.81	.68	.80
Biphenyl	.30	.52	.49	.40	.48
Acenaphthene	.26	.21	.23	.17	.20
Acenaphthylene	1.32	2.55	2.82	2.15	2.43
Dibenzofuran	.99	1.90	2.09	1.55	1.81
Fluorene	1.10	2.05	2.41	1.84	1.99
Phenanthrene	4.06	5.93	8.28	5.95	5.68
Anthracene	.88	.78	.96	.76	.76
Carbazole	.40	.20	.53	.19	.23
Fluoranthene	1.80	1.61	3.57	1.68	1.53
Pyrene	1.09	.53	2.10	.54	.50
1,2-Benzanthracene	.05	.61	.09	.034	.030
Chrysene	.19	1.25	.28	.011	.29

Studies were also done in order to determine how much creosote was migrating over a 30-day period. These studies employed a 4-liter glass beaker and were conducted under carefully controlled temperature conditions. Three sets of experiments were done: fresh water with an unaged sample of treated wood, sea water with an unaged sample of treated wood, and sea water with an aged sample of treated wood. The results are summarized for the three systems in Table 11. The same trends that were observed over the three-day time period (Tables 5 - 7) were also evident for the 29-day time period. The unaged wood samples in fresh water produced higher concentrations of PAH than the unaged samples in sea water. Unaged samples also produced higher concentrations of PAH than the aged samples in sea water. However, the differences among the three systems were much less over the longer time periods than for the short time periods. For example, at 16 days the total PAH from the unaged sample in fresh water was 1709 ppb; the total PAH from the unaged sample in sea water was 1225 ppb; and the total from the aged sample in sea water was 316 ppb. These results also indicate that after five days the PAH concentration from the treated wood was not dependent on time. In most cases over 60% of the observed PAH was obtained after 5 - 12 days. The concentration increased only slightly--or in some cases actually decreased--at longer time periods.

Long-term studies were also done using a 300-gallon stainless steel tank. The major difference between the tank runs and the beaker runs was the ratio of the wood surface area to the volume of water. In the beaker runs the ratio of wood surface area (cm^2) to the volume of water (liters) was 21.7 - 25.3. In the larger unit the ratio varied from 0.54 - 2.71. Two types of studies were done in the large vessel: migration of creosote components from unaged marine pilings in sea water

Table 11. Migration of Creosote Components from Wood over a 29-day Period.^{a,b}

Compound	Fresh Water Unaged Sample (ppb) Days					Sea Water Unaged Sample (ppb) Days					Sea Water Aged Sample (ppb) Days				
	5	12	16	23	29	5	12	16	23	29	5	12	16	23	29
Naphthalene	65	74	64	42	24	-	5.4	8.8	17	24	-	-	1.1	7.9	23
2-Methylnaphthalene	77	107	115	65	62	33	42	91	48	59	9.3	2.8	2.8	28	31
1-Methylnaphthalene	41	90	108	86	88	14	38	100	82	88	5.3	2.3	1.6	116	151
Biphenyl	34	36	43	30	29	18	20	30	21	19	5.8	3.7	3.8	5.6	7.0
Acenaphthene	34	56	68	53	56	27	46	64	53	45	3.4	20	21	-	41
Acenaphthylene	182	81	280	204	189	106	143	175	135	120	55	71	77	99	142
Dibenzofuran	134	168	171	143	129	88	113	134	101	100	38	51	50	55	88
Fluorene	145	176	193	163	157	84	113	128	105	105	44	66	52	36	92
Phenanthrene	277	360	374	369	369	127	227	279	253	281	53	66	25	63	105
Anthracene	80	130	132	124	90	50	84	91	94	102	27	44	38	47	58
Carbazole	53	83	93	69	98	32	55	60	76	85	1.8	16	19	9.3	25
Fluoranthene	35	46	41	76	52	23	35	39	50	50	20	30	20	24	28
Pyrene	19	26	25	42	27	16	13	19	22	25	-	16	11	9	14
1,2-Benzanthracene	2.1	2.8	1.6	3.1	4.0	0.8	1.4	6.0	1.5	4.7	16	19	2.1	16	3.6

^aSamples used had: Exposed Surface Area = 58.0 - 62.7 cm².
 Water Volume = 3500 ml.
 Temperature = 30.0 ± 0.5°C.

^bEach value represents an average of two runs.

and migration of creosote components from aged marine pilings in sea water. The results are summarized in Tables 12 - 16.

The concentration of the PAH reached a maximum value and then decreased. For example, after 72 hours the PAH migration from an unaged sample reached a level of 432 ppb (Table 12) and after 288 hours the concentration had decreased to 156 ppb. Larger decreases were observed with the aged samples. For example, after 24 hours the total concentration of the PAH reached 97.4 ppb and then decreased to 26.2 ppb after 480 hours (Table 15). The same general trends were observed for all aged samples (Tables 14 - 16). The most likely explanation for this decrease is a rapid degradation of the solubilized PAH. This reduction could be due to chemical or biological degradation; however, the fact that the concentration initially increased to a maximum and then rapidly decreased, plus the fact that the maximum rate of PAH decomposition occurred only when low concentrations of PAH were present, strongly indicates biological degradation.

Reports of microbial assimilation of hydrocarbons are common. Zobell et al. (8) observed the oxidation of naphthalene and other products of coal origin by marine organisms. Similarly, Gray and Thornton (9) described several species of Pseudomonas that have the ability to utilize naphthalene.

The biodegradation of naphthalene, creosote, and naphthalene-enriched creosote applied to wood piling was studied by Colwell (10). He reported that naphthalene-degrading bacteria colonized new wood piling within hours when they were installed in the coastal waters of Puerto Rico. Similarly, Traxler (11) isolated 15 different genera of hydrocarbon-utilizing bacteria from low-temperature waters and sediments.

Table 12. Migration of Creosote from an Unaged Marine Piling.^a

Compound	Concentration (ppb)				
	Time (Hours)				
	24	48	72	168	288
Naphthalene	22	2	--	--	--
2-Methylnaphthalene	4.9	4.9	3.7	0.9	0.7
1-Methylnaphthalene	1.6	0.2	14	12	13
Biphenyl	7.7	3.2	18	18	7.0
Acenaphthene	6.2	4.2	7.4	5.4	--
Acenaphthylene	39	15	53	36	5.1
Dibenzofuran	93	75	123	76	41
Fluorene	37	28	61	74	38
Phenanthrene	65	47	93	93	14
Anthracene	13	7.8	24	17	19
Carbazole	15	8.4	21	21	13
Fluoranthene	4.8	6.9	8.2	10	4.0
Pyrene	3.2	5.8	5.4	5.4	1.2
	202	264	431	351	106

^aSample used had: Exposed Surface Area = 3375 cm².
Volume of Sea Water = 250 gallons.
Temperature = 18 - 20°C.

Table 13. Migration of Creosote from an Unaged Marine Piling.^a

Compound	Concentration (ppb)							
	Time (Hours)							
	8	16	24	48	120	240	480	600
Naphthalene	--	--	--	--	3.1	4.9	3.3	--
2-Methylnaphthalene	0.6	2.3	1.9	7.2	4.9	13	13	3.5
1-Methylnaphthalene	0.4	1.4	1.2	3.5	4.0	9.4	8.8	.05
Biphenyl	3.6	2.0	2.1	8.8	9.3	32	2.6	1.6
Acenaphthene	2.0	9.1	4.5	7.6	10	10	12	5.2
Acenaphthylene	17	20	3.5	8.1	110	19	178	80
Dibenzofuran	16	25	3.5	66	95	80	47	33
Fluorene	24	38	4.2	78	118	116	71	58
Phenanthrene	82	4.2	17	197	243	170	79	154
Anthracene	--	--	--	--	39	--	20	--
Carbazole	5.4	6.7	3.0	13	11	3.1	2.6	3.0
Fluoranthene	16	20	15	28	25	40	31	37
Pyrene	--	15	3.2	13	15	16	16	19
	167	140	50	430	107	513	484	349

^aSample used had: Exposed Surface Area = 2565 cm².
Volume of Sea Water = 210 gallons.
Temperature = 17 - 19°C.

Table 14. Migration of Creosote from Aged Marine Pilings.^a

Compound	Concentration (ppb)									
	Time (Hours)									
	8	16	24	32	40	48	72	120	240	480
Naphthalene	--	--	--	--	--	--	--	--	--	--
2-Methylnaphthalene	4.8	0.6	1.1	0.2	--	--	--	--	--	--
1-Methylnaphthalene	6.9	0.6	2.8	1.1	--	--	--	--	--	--
Biphenyl	3.5	0.5	0.2	.17	--	.11	--	--	--	--
Acenaphthene	4.2	4.7	4.8	4.6	1.7	2.1	1.1	0.9	--	--
Acenaphthylene	62	130	74	61	16	4.7	0.2	0.5	2.3	0.8
Dibenzofuran	44	52	60	50	11	24	16	1.9	0.7	1.6
Fluorene	65	95	102	101	42	68	49	1.0	1.6	1.4
Phenanthrene	186	302	262	184	8.5	81	23	1.3	--	--
Anthracene	31	39	37	37	12	23	14	2.2	--	--
Carbazole	2.2	2.6	5.7	4.7	8.0	2.0	7.6	1.0	0.8	--
Fluoranthene	54	52	47	45	54	54	49	64	37	29
Pyrene	31	33	31	30	37	32	33	18	13	--
1,2-Benzanthracene	18	--	3.0	3.5	6.0	3.1	0.9	0.5	0.6	0.9
	512	714	631	523	146	244	123	90	57	34

^aSample used had: Exposed Surface Area = 513.5 cm².
Volume of Sea Water = 251 gallons.
Temperature = 21°C.

Table 15. Migration of Creosote from Aged Maring Pilings.^a

Compound	Concentration (ppb)							
	Time (Hours)							
	8	16	24	48	72	120	240	480
Naphthalene	2.1	--	--	--	--	--	--	--
2-Methylnaphthlene	2.1	0.2	0.8	--	--	--	--	--
1-Methylnaphthlene	1.2	1.0	0.3	--	0.6	--	--	--
Biphenyl	1.9	1.9	1.3	--	--	--	--	--
Acenaphthene	1.8	2.1	1.3	--	--	--	--	--
Acenaphthylene	22	32	21	--	0.2	0.4	0.4	0.4
Dibenzofuran	14	19	13	0.7	0.3	0.3	--	0.6
Fluorene	25	29	28	--	0.5	1.7	0.9	9.1
Phenanthrene	69	36	16	1.6	3.4	--	--	--
Anthracene	--	--	5.6	--	--	--	--	--
Carbazole	3.3	3.7	5.9	--	4.0	0.7	1.1	2.3
Fluoranthene	0.5	0.1	0.7	--	2.3	6.4	7.4	5.0
Pyrene	9.4	9.3	--	7.4	12	--	2.5	6.6
1,2-Benzanthracene	--	--	3.5	--	29	--	94	2.2

^aSample used had: Exposed Surface Area = 1471 cm².
Volume of Sea Water = 229 gallons.
Temperature = 18 - 20°C.

Table 16. Migration of Creosote from Aged Marine Pilings.^a

Compound	Concentration (ppb)					
	Time (Hours)					
	8	16	24	168	240	600
Naphthalene	--	--	--	--	--	--
2-Methylnaphthalene	0.22	0.21	--	--	--	--
1-Methylnaphthalene	0.14	--	--	--	--	--
Biphenyl	.52	0.68	.61	.11	.15	--
Acenaphthene	.77	0.81	.52	.26	--	--
Acenaphthylene	4.5	6.6	4.8	.30	.29	.80
Dibenzofuran	4.6	6.4	3.3	.49	.61	--
Fluorene	11	15	10	.65	.44	.43
Phenanthrene	31	21	.53	--	--	--
Anthracene	8.8	7.9	3.1	.84	--	--
Carbazole	6.2	1.4	.76	.52	--	.49
Fluoranthene	0.5	16	14	4.8	--	6.5
Pyrene	6.1	14	13	--	--	--

^aSample used had: Exposed Surface Area = 585.6 cm².
Volume of Sea Water = 203 gallons.
Temperature = 18 - 20°C.

All of the isolates metabolized naphthalenic and aliphatic hydrocarbons.

In studies conducted by Lee and Anderson (12), it was observed that concentrations of naphthalenes added to a 1/4-scale CEPEX enclosure declined by 50% within 24 hours and gradually declined to background levels over a period of 20 days. Reductions were attributed by the authors to adsorption by sinking phytoplankton and microbial degradation.

Different paraffinic and aromatic ^{14}C -labeled hydrocarbons added to estuarine and off-shore water samples were monitored for $^{14}\text{CO}_2$ production after incubation periods of 6 to 96 hours by Lee and Ryan (13). Naphthalene had high degradation rates relative to higher-molecular-weight hydrocarbons. Rate of degradation was reported to be affected by season, tide, total hydrocarbon concentration, and incubation time.

Zobell et al. (8) noted that, as a rule, hydrocarbons having a boiling point above 150°C are assimilated more readily by bacteria than those having a lower boiling point. They reiterated what others have reported; namely, that bacteria found in a marine environment are capable of utilizing a wide variety of hydrocarbons, including anthracene and naphthalene. All samples of sediment which they examined contained hydrocarbon-oxidizing bacteria, regardless of distance from land, water depth, or core depth.

CONCLUSIONS

The amount of creosote that migrates from a marine piling is extremely small. By using the information in Table 6, one can calculate an estimate of the total PAH that migrate from a piling. By assuming that the piling is 10 feet long and has a total surface area

of 15,000 cm², the rate of creosote migrating from the piling would be in the range of 77 - 147 grams per year. This small amount, plus the fact that the PAH apparently are rapidly broken down in water, indicates that the quantity of PAH that migrates from creosote-treated pilings into sea water should have only a minimal effect on the environment, if, indeed, it has any effect at all.

Some more specific conclusions from this study are:

1. The major PAH migrating from wood are naphthalene, phenanthrene, acenaphthylene, dibenzofuran, fluorene, and 2-methylnaphthalene. These six PAH make up approximately 70 - 80% of the total PAH migrating from treated wood.
2. Higher concentrations of PAH migrate from treated wood in fresh water than in sea water. This effect is not due to the decreased solubility of the creosote components in sea water, but is apparently due to some change in the wood caused by the sea water. In general it was found that sea water reduced the rate of migration of the PAH by approximately 50%. This effect was noted at temperatures from 20 - 40°C.
3. Lower concentrations of creosote migrate from aged marine pilings than unaged pilings. This phenomenon is not due to the lower levels of creosote in the aged pilings but apparently is due to changes in the availability of the creosote on the surface of the wood.
4. Long-term studies (15 - 30 days) that employed a 300-gallon tank indicate that the concentration of PAH reach a maximum after a short period of time, then decrease rapidly due to biological or chemical decomposition.

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